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FINAL REPORT

for

REVIEW OF "PHASE I TREATABILITY STUDY WORK PLAN, PERCHLORATE IN GROUNDWATER" AND "TECHNOLOGY SCREENING FOR THE TREATABILITY OF PERCHLORATE IN GROUNDWATER" REPORT FOR THE SAN GABRIEL BASIN SF, BALDWIN PARK OPERABLE UNIT (BPOU)

on

CONTRACT NO. 68-C7-0008
WORK ASSIGNMENT NO. 1-01, TASK 3

to

NATIONAL RISK MANAGEMENT RESEARCH LABORATORY
U.S. ENVIRONMENTAL PROTECTION AGENCY

November 13, 1997

1.0 Introduction

Perchlorate concentrations in excess of California mandatory action levels have been discovered in a groundwater plume at the San Gabriel Basin, Baldwin Park Operable Unit (BPOU). An effort to identify suitable treatment technologies was undertaken, and a report titled "Technology Screening for the Treatability of Perchlorate" was produced, which identified a biochemical treatment technology as the most likely candidate for use at the site. In light of the recommendation for a biological approach, a report was prepared titled "Phase I Treatability Study Work Plan, Perchlorate in Groundwater," to serve as a guide to conducting a treatability study for evaluating the biological treatment option at the site.

2.0 Objectives and Scope

The purpose of Task 03 under this work assignment (WA) is to provide a technical review of the technology screening and treatability study documents and provide results of the review in the form of written comments. Subsequent to submitting this report, Battelle will participate in a conference call with the Remedial Project Manager (RPM), Wayne Praskins, to discuss the documents and their potential utility for selecting appropriate treatment technologies for the BPOU.

3.0 Technical Approach

This task involves the technical review of the technology screening and treatability study documents referenced above. This technical review was conducted in light of comments provided by Mr. Wayne Praskins in a conference call conducted on October 27, 1997. The review addresses specific questions posed by the RPM, including whether modifying the alcohol feed rate but not other parameters during Phase I of the treatability test is an appropriate strategy, whether steps can be taken during Phase II to optimize the process, whether ion exchange is the next-best treatment technology after biological treatment, whether there are specific resins and regenerates that should be investigated, whether there are catalysts that should be investigated for possible use in a catalyzed chemical reduction approach, whether carbon types other than coal-based should be tried for the granular activated carbon (GAC) treatment units, and whether there are other technologies not mentioned in the technology screening report that merit attention.

4.0 Results of Review

As requested in the subject Technical Directive, Battelle reviewed the documents titled "Final Phase 1 Treatability Study Work Plan Perchlorate in Groundwater Baldwin Park Operable Unit San Gabriel Basin" and "Draft Technology Screening for the Treatability of Perchlorate in Groundwater Baldwin Park Operable Unit San Gabriel Basin." The purpose of this letter report is to answer the questions proposed in the Technical Directive and to summarize Battelle's concerns regarding the approach and information provided in the these two documents.

Final Phase 1 Treatability Study Work Plan
Perchlorate in Groundwater
Baldwin Park Operable Unit
San Gabriel Basin

Question 1. Is the methodology described in the Work Plan a good one?

Response: The overall approach presented in this document is to test the existing pilot system at Aerojet's Sacramento facility. The feed water will be formulated to simulate the water at the BPOU by selecting and blending water from various wells at the Sacramento site to achieve appropriate perchlorate concentrations, then adding nitrate as needed. It is suggested that the other competing electron acceptors, especially sulfate, also be amended into the feed water. While it would not be suggested that any remediation technology be tested using anything other than the actual matrix to be tested, it is assumed that this phase of the study is being conducted to simply answer the question of can the biological process achieve the 18 μg/L treatment level.

Phase II testing will involve pilot testing at the Baldwin Park site and the tests should be designed to determine if the process works on that specific groundwater and to collect the data needed for scale-up purposes.

Question 2. Is it appropriate to increase the alcohol feed rate but not vary any other parameter?

Response: It may be appropriate depending on how much is understood about the microbial utilization of perchlorate and microbial metabolic interactions within the reactor environment. It is mentioned in the report that Aerojet has already tested and developed their biological process to some extent, achieving perchlorate reductions down to the 100 μg/L level. It is assumed that the effect of parameters such as pH, temperature, nutrient concentrations, biomass concentration, fluidization, contact time, and electron donor (alcohol) have all been investigated and that the technology developers are confident with the design parameters they have chosen. It appears that they believe that if enough electron donor is supplied, eventually all of the electron acceptor will be utilized.

Electron donors are used in order of decreasing redox potential. The typical order is oxygen followed by nitrate then iron then sulfate and finally to methanogenesis. While it has been demonstrated that chlorate falls between nitrate and sulfate, it is unknown where perchlorate fits in among the electron acceptors. While feeding more substrate may be applicable for exhausting the electron acceptors such as oxygen, nitrate, and iron, that do not require the very low redox levels, competition for substrate for sulfate reduction and methanogenesis can become predominant at high substrate concentrations. Depending on where perchlorate falls, it may be necessary to overcome the sulfate demand while minimizing the competition with methanogenesis. It appears from the lack of consideration given to sulfate in the experimental plan that Aerojet may have determined that perchlorate will be utilized before sulfate and that the alcohol feed rate can be adjusted to maintain the redox level in the reactor above sulfate reducing levels.

Varying only the alcohol feed rate may result in failure to achieve the desired treatment level.

Question 3. If Phase I demonstrates reduction of perchlorate to below 18 μg/L, are there any suggestions for Phase II scale-up to optimize the process?

Response: Proving that perchlorate concentrations of 18 μg/L can be achieved using the biological process as described in Phase 1 in the referenced document is a very preliminary step in developing a cost effective and reliable technology for achieving the objectives at Baldwin Park. Phase I will simply provide information on the potential for incorporating this technology into the finalized treatment process design. It is imperative that the technology be pilot tested in the location and with the water that is to be treated during implementation of the technology. This appeared to be the focus of the pilot-scale tests described for Phase II. There was not much information provided in the Work Plan on how Phase II would be conducted, but the overall objectives were appropriate. Pilot-scale testing must focus on optimizing system performance for the specific site conditions at Baldwin Park. This will entail varying operating parameters such as reactor loading, substrate selection and addition, biomass retention, and pH adjustment, if necessary. In addition, any required pretreatment and/or post treatment needs to be included and these processes need to be optimized and tested for reliability. The reliability of all of these processes is an extremely important issue when developing treatment processes for distribution in drinking water supplies.

Draft Technology Screening for the Treatability of Perchlorate in Groundwater
Baldwin Park Operable Unit
San Gabriel Basin

Question 1. Do you agree with the consultant's recommendation that ion exchange is the next best technology worthy of study?

Response: Actually we disagree with the ranking of the technologies as a whole. We ran through a quick evaluation of the technologies presented in this document and followed the same scoring system. We selected the same top six technologies that were selected in the report, but our order of preference was somewhat different. The technologies were selected in preferential order as reverse osmosis, ion exchange, electrodialysis, biochemical reduction, capacitative deionization, and finally activated carbon. Reverse osmosis and ion exchange scored very close, so we would agree that either of these technologies should be considered.

The screening document was very biased against the technologies competing against biochemical reduction. There was no mention of the major concerns associated with using the described biological approach for producing drinking water. One concern is the potential for upset of the biological perchlorate reduction process. Variations in any number of operational parameters as well as mechanical failures and downtime can result in decreased performance in the bioreactor and cause elevated perchlorate concentrations in the water being injected into the potable water supply. Another concern is the potential for introducing residual methanol, metabolic byproducts, or unwanted microorganisms into the drinking water supply. While the described process did include filtration and disinfection, these processes may not eliminate these concerns, and disinfection with chlorine could result in unwanted reactions such as trihalomethane formation. While biochemical reduction has been shown effective by researchers at Aerojet, Tyndall Air Force Base in Florida, and the University of Southern California for perchlorate reduction in contaminated groundwater and wastewater, we felt that more consideration must be given to applying the technology for potable water production.

We felt that a combination of technologies would provide a more reliable and cost-effective treatment process for producing potable water. While it is true that the three top-rated technologies would not result in perchlorate destruction, the technologies are more mature and better understood, and their would be less risk of upset than with the biological process. There are many biological wastewater treatment plants and many of these suffer from upsets that adversely affect treatment performance. While many of these upsets are caused by perturbations in the wastewater feed, many are due to poor operating practices and/or human error. Although any treatment technology is subject to operator error, experience has shown that biological processes are more prone to upset and/or degreased system performance. In the case of the biological process described in this Work Plan, this could result in not meeting the required perchlorate treatment level and/or introducing residual methanol and/or disinfection byproducts into the drinking water supply.

While we feel that there is a role for biological reduction in the overall treatment process, we felt that a combined technology approach would provide a more reliable and effective process for removing the perchlorate while minimizing some of the risks of any single technology. We felt that it would be beneficial to apply technologies that can effectively remove perchlorate while reducing the volume of water that needs to be treated for perchlorate destruction. Reverse osmosis, ion exchange, and electrodialysis are effective at doing this. Applying the biological process to the reject streams from this process would minimize chemical usage, and moving the biological process to a side stream position would remove the risks associated with upset or decreased performance. The water from the biological process would be filtered and returned to the head of the treatment process. One additional note, ion exchange regenerant streams contain a high level of salts and the water activity may be too low for biological treatment.

We agreed that the capacitative deionization technology is too immature to consider for full-scale production of potable water. Further developments of this technology may increase its applicability. Activated carbon was excluded for the reasons discussed below.

Question 2. Can you suggest resins and regenerates that should be evaluated?

Response: After talking to several ion exchange resin vendors, it became apparent that the technology has not been developed for perchlorate removal. While the companies agreed that it is worth investigating, they all suggested bench-scale experiments to determine the effectiveness of their resins. The major concerns were the potential for resin oxidation by the perchlorate, the competition for adsorption sites by other anions, and the uncertainty of the regeneration of the resins. These concerns would be addressed through bench-scale testing.

The water chemistry data provided in Table 6-7 shows that there are significant levels of sulfate, nitrate, and chloride in the water. These anions would compete with perchlorate for exchange sites on most ion exchange resins and could require unacceptably short run times. Fortunately, there are resins that preferentially exchange monovalent anions that are more selective for nitrate over sulfate. One such example is ResinTech's SIR-100. These resins may provide for preferential removal of nitrate and perchlorate and may extend run times. A major concern with the selection of a resin is its resistance to oxidation and the ability to exchange the perchlorate during regeneration. The major resin manufacturers will either provide resins free of charge for testing or they will do the testing for you.

With regards to the regenerants, sodium chloride, sodium bicarbonate, and sodium hydroxide are the most common and, depending on the resin, any one of these may be applicable. The resin manufacture's should recommend the regenerant of choice. What we have observed in our experience with ion chromatography is that perchlorate is more difficult to replace than either sulfate or nitrate. While it may take a higher strength regenerant to displace the perchlorate, it may be possible to preferentially remove these other anions, then remove the perchlorate. Bench-scale tests should be collected during the resin selection process.

Question 3. Can you provide any advice on test protocols?

Response: We recommend using a straightforward column testing protocol using groundwater from the San Gabriel Basin. The water should be subjected to any pretreatment that the water would be exposed to during implementation. The protocol must include developing breakthrough curves at varying influent feed compositions and flow rates. This is done by packing the resins into small columns and pumping groundwater through the columns at a known flow rate. The effluent from the column is collected using a fraction collector and analyzed for all of the anions of concern. The resin is regenerated, then put in line, and a second breakthrough curve is developed. This process may be repeated several times to generate several breakthrough curves following several regeneration cycles. The breakthrough curves provide information required to determine the exchange capacity for perchlorate and other ions of concern, as well as the run times that can be expected. They are also compared to determine the regenerability and the expected life of the resins.

Question 4. Can you suggest catalysts that should be tested to see if catalyzed chemical reduction would work?

Response: We have tested zero-valent iron, ferrous iron, and sodium dithionite for their capacity to reduce perchlorate in contaminated water. None of these provided any reduction. This result was attributed to the fact that these materials could not overcome the high activation energy required to reduce the perchlorate. Research has been conducted investigating bi-metallic systems such as palladized iron and zinc-iron combinations. These combinations have been shown to overcome the activation energy constraints of other chemical reactions, but would most likely not work on perchlorate. The catalysts that would have the greatest potential for destroying perchlorate appear to be Ru (II), V (II), V (III), and Ti (III). Ru is very expensive since its occurrence in the earth's crust is rarer than platinum. $TiCL_3$ is more common, but it is readily oxidized by air. Ti_2O_3 is fairly inert and would be one possibility, but it may react with perchlorate to form aqueous Ti(III). One problem associated with using these materials for treating water for potable use is that the metals can tend to leach from the beds and may pose an additional treatment requirement. Because the goal is to produce potable water, the best candidates may be the vanadium compounds because vanadium is considered an essential micronutrient. If economics necessitate recovery of the metal, the project would be challenging.

Question 5. Would other types of GAC other than coal-based carbon last longer or be as efficient?

Response: It is possible that granular activated carbon from sources other than coal could have higher mechanical strength properties, and less carbon may be lost to attrition during regeneration and handling. However, there may be a loss in adsorptive capacity with some of the harder carbons, as they tend to be less porous and have less adsorption sites. GAC produced from coconut shells tends to have a higher density and finer pore size distribution, making it a good candidate for adsorbing small molecules. The more typical application for this type of activated carbon is for gas-phase treatment, because of the mass transfer limitations in aqueous treatment. Any added capacity may be overcome if there are organic or other larger molecules in the groundwater.

We would not recommend considering the use of activated carbon for treating perchlorate-contaminated groundwater to produce potable water. The data show that the capacity for perchlorate adsorption is low. Research has shown that the adsorption of chlorate and other anions is weak and reversible, and it would be expected that perchlorate adsorption would be similar. This means that the breakthrough would be rapid and there would be the potential for feedback into the treated water. This could result in excessive perchlorate getting into the drinking water distribution system.

Question 6. Do you have any idea on how pretreatment with ozone/peroxide increased the removal of perchlorate?

Response: We can offer two possible explanations for the increased perchlorate removal. First it is possible that the ozone and/or peroxide could have reacted with organic carbon in the water. Organic carbon has been shown to reduce the adsorptive capacity of chlorate (Gonce and Voudrias, 1994). If there was organic matter in the water that was oxidized, the net effect would be greater perchlorate removal. A second possibility is that some oxidation of the carbon occurred, creating additional adsorption sites. While neither ozone nor peroxide provide a long-lived residual in water, the time between water treatment and carbon contact may have been short enough so as to allow some reactivity with the carbon. This could have resulted in production of additional adsorption sites.

Question 7. Address any other technologies that should be considered.

Response: There are two concerns for selecting technologies for this specific application. These concerns are the volume of water that needs to be treated and the low perchlorate concentration that needs to be achieved. The technologies included in the list of 6 are the best technologies currently available for consideration. As mentioned in our comments above, we believe that the order of ranking may have been biased towards biological reduction and that the approach focussed on selection of one technology when a combination of technologies may be a more appropriate approach for producing potable water. As far as developing technologies are concerned, the capacitative deionization technology appears most promising.

Reference

Gonce, N., and E.A. Voudrias. 1994. "Removal of Chlorite and Chlorate Ions from Water Using Granular Activated Carbon." *Wat. Res.* *28*(5): 1059-1069.

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